

UNCLASSIFIED

AD

407984

19991117172

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

63-4-2

ASD-TDR-63-208

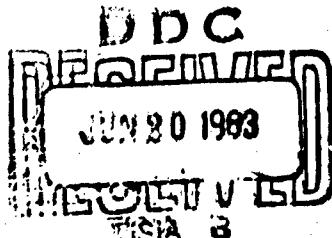
4071984  
CATALOGED BY DDC 984  
AS AD No. \_\_\_\_\_

RESEARCH AND DEVELOPMENT TO INVESTIGATE THE MICROSTRUCTURE  
OF THE INTERNAL MAGNETIC FIELD IN FERRO-, FERRI-,  
AND ANTIFERROMAGNETIC SOLIDS

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-63-208  
April 1963

Directorate of Materials and Processes  
Aeronautical Systems Division  
Air Force Systems Command  
Wright-Patterson Air Force Base, Ohio

Project No. 7371, Task No. 737103



(Prepared under Contract No. AF-33(657)-8462  
by the General Electric Company, Schenectady,  
New York; D.S. Rodbell, T.W. Moore, and I.S.  
Jacobs, authors)

Reproduced From  
Best Available Copy

## NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Qualified requesters may obtain copies of this report from the Armed Services Technical Information Agency, (ASTIA), Arlington Hall Station, Arlington 12, Virginia.

This report has been released to the Office of Technical Services, U.S. Department of Commerce, Washington 25, D.C., for sale to the general public.

Copies of this report should not be returned to the Aeronautical Systems Division unless return is required by security considerations, contractual obligations, or notice on a specific document.

## FOREWORD

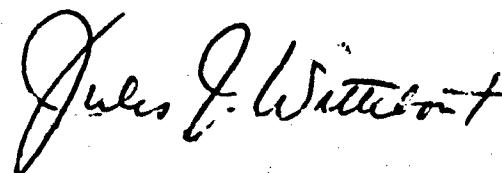
This report covers work carried out in the Metallurgy and Ceramics Research Department of the General Electric Research Laboratory under USAF Contract No. AF-33(657)-8462, entitled "Research and Development to Investigate the Microstructure of the Internal Magnetic Field in Ferro-, Ferri-, and Antiferromagnetic Solids." This contract was initiated under Project 7371, "Applied Research in Electrical, Electronic, and Magnetic Materials," Task No. 737103, "Applied Research on Magnetic Materials." The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with W. G. D. Frederick acting as project engineer.

This Final Report is concerned with the period 1 March 1962 to 31 January 1963. The principal participants in this research were D. S. Rodbell, T. W. Moore, I. S. Jacobs, and W. L. Roth. Many colleagues provided frequent stimulation and encouragement throughout this work.

## ABSTRACT

A number of research projects dealing with fundamental interactions and the microstructure of internal fields in selected magnetic materials were initiated or continued from an earlier contract (see ASD Technical Report No. 61-630). (a) The magnetocrystalline anisotropy and electron spin resonance in single crystals of gadolinium metal are being investigated by microwave techniques, and correlated to static field mechanical torque results. (b) The thermal expansion anomalies near the Curie points of the ferromagnetic metals, gadolinium and nickel (whose anomalies are of opposite sign), have been analyzed in terms of recent theoretical work which considers the interatomic separation dependence of the magnetic exchange. (c) An investigation to look for coherency strains in the cobalt particles precipitated in a copper-cobalt alloy has been initiated using the nuclear resonance frequency of the particles as a sensitive probe. (d) The same alloy system is under study by ferromagnetic resonance techniques with a view to understanding its magnetic annealing, i.e.: Are the particles' shapes affected by heat treatment in an externally applied magnetic field? (e) The nuclear magnetic resonance of both Mn and As in the compound MnAs has been observed, and several questions of fundamental importance to an understanding of its hyperfine fields are raised by the results. (f) An exploratory study of electron tunneling into several ferromagnetic alloy systems has revealed new behavior that may cast light on current studies of the band structure of these alloys. (g) A study of the thermal expansion of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has been used to resolve questions concerning its Néel point and to predict the pressure dependence thereof. (h) Research into the antiferromagnetic behavior of FeCO<sub>3</sub>, initiated earlier, has been continued with the identification of a metamagnetic transition between 100 and 200 kOe. (i) An investigation into the magnetization behavior of antiferromagnetic CoCl<sub>2</sub> has been started. (j) Public presentation of the earlier work on magnetic exchange and structure in lanthanum manganite perovskites has been carried nearer to completion.

This technical documentary report has been reviewed and is approved.



JULES I. WITTEBORT  
Chief, Thermophysics Branch  
Physics Laboratory  
Directorate of Materials and Processes

## TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION.....	1
1. Anisotropy and Spin-Resonance in Gadolinium Metal .....	1
2. Thermal Expansion Anomaly in Gadolinium and Nickel.....	5
3. Nuclear Resonance of f. c. c. Cobalt Particles Precipitated in a Copper-Cobalt Alloy .....	9
4. Magnetic Annealing in Cu-2 Per Cent Co Alloys .....	9
5. Nuclear Resonance in MnAs .....	9
6. Electron Tunneling into Ferromagnetic Metals .....	11
7. Thermal Expansion and the Néel Temperature of Antiferromagnetic $\alpha\text{-Fe}_2\text{O}_3$ .....	11
8. Antiferromagnetic Behavior of $\text{FeCO}_3$ .....	16
9. Antiferromagnetism of $\text{CoCl}_2$ .....	23
10. Magnetic Structure and Exchange in the Lanthanum Manganite Perovskites.....	25

RESEARCH AND DEVELOPMENT TO INVESTIGATE  
THE MICROSTRUCTURE OF THE INTERNAL MAGNETIC FIELD  
IN FERRO-, FERRI-, AND ANTIFERROMAGNETIC SOLIDS

D. S. Rodbell, T. W. Moore, and I. S. Jacobs

INTRODUCTION

The guiding theme of the research in this report was the study of fundamental interactions and the microstructure of the internal fields in selected magnetic materials by means of magnetic resonance techniques and high-strength magnetic fields, with other experimental and analytical tools as needed to facilitate the research. These are described as separate studies in the material which follows.

1. Anisotropy and Spin-Resonance in Gadolinium Metal (DSR, TWM)

The rare-earth metals provide a largely unexplored area in which to extend and augment our understanding of fundamental properties of magnetic materials. It is from this viewpoint and stimulated by the availability of these elements that our attention has focused upon them.

Single crystals of gadolinium were grown by J. W. Rutter and T. Sawyer of the GE Research Laboratory using a standard ("seed-pulling") technique. In cooperation with C. D. Graham, of the Laboratory, coin-shaped disks of desired orientation were machined. (Dr. Graham has been studying the magnetocrystalline anisotropy of some of these samples by measurement of the mechanical torque on a sample as it is rotated in a magnetic field. We are indebted to him for informing us of his experimental results prior to publication.) As mentioned in ASD Technical Report No. 61-630, the initial experiments in this area done under this contract established that the easy axis of magnetization near the Curie temperature (16°C) is along the "c" axis of the hexagonal crystal, while at lower temperature near 77°K the basal plane becomes the preferred orientation of the magnetization. Graham has confirmed these initial observations with his torque measurements. We have been recently studying the temperature dependence of the magnetocrystalline anisotropy of these crystals by direct magnetization measurements and by electron-spin resonance at 34 kMc/s. In the analysis of the resonance data, it is necessary to know the magnetization of the sample and since samples may differ from various causes (impurities, <sup>†</sup>

---

Manuscript released by the authors April 1963 for publication as an ASD Technical Documentary Report.

<sup>†</sup>An analysis of our samples is given here as impurities in parts per  $10^6$ .  
Silicon--100; calcium--3500; iron--350; copper--100; nickel--100;  
aluminum--1000; tantalum--800; oxygen--2000.

strain, etc.), we have made direct measurements on our samples at three fixed temperatures. These data are given in Table I:

TABLE I

Temp (°K)	Ms emu/cc
77	2085 $\pm$ 20
273	920 $\pm$ 20
300	(Paramagnetic $1/\chi_0 = 4.25 \pm 0.25$ Oe cc/emu)

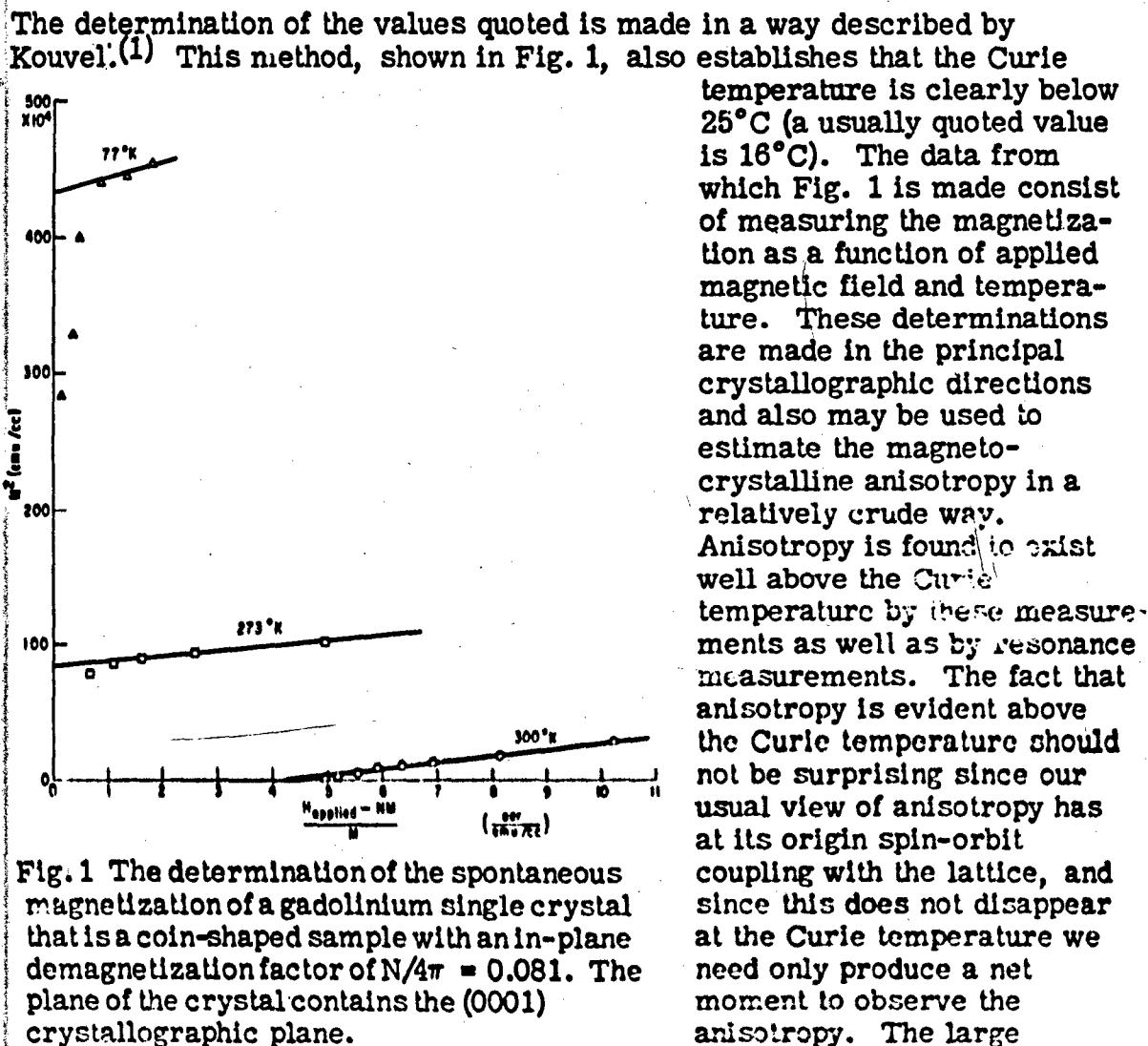


Fig. 1 The determination of the spontaneous magnetization of a gadolinium single crystal that is a coin-shaped sample with an in-plane demagnetization factor of  $N/4\pi = 0.081$ . The plane of the crystal contains the (0001) crystallographic plane.

susceptibility available just above the Curie temperature allows such a moment to occur and to reflect the anisotropy present.

In analyzing the electron-spin resonance experiments, we make use of the expression (1) which is the usual "Kittel relation" for metals.

$$\left(\frac{\omega}{\gamma}\right)^2 = (H_i + 4\pi M) H_i^* \quad . \quad (1)$$

In this expression  $\gamma = ge/2mc$  and the internal fields  $H_i$  and  $H_i^*$  include demagnetizing and anisotropy terms as well as the externally applied field. Because of the relatively large saturation magnetization [ $4\pi M_s(0) = 27,000$  gauss] and large resonance line widths, these experiments are being performed at 34 kMc/s so that the resonance will occur at sufficiently high applied fields to fully resolve the lines and to separate them from domain wall phenomena at low fields. We write the anisotropy energy as:

$$E_A = K_1 \sin^2\theta + K_2 \sin^4\theta + K_3 \sin^6\theta + \dots \quad (2)$$

where  $\theta$  is the angle between  $\bar{M}$  and the c-axis and use the method of Artman<sup>(2)</sup> to obtain

$$H_i = H + \frac{2K_1}{M} \cos^2\theta + \frac{K_2}{2M} \sin^2 2\theta - NM \quad (3)$$

$$H_i^* = H + \frac{2K_1}{M} \cos 2\theta + \frac{2K_2}{M} (\sin^2 2\theta + 2\sin^2\theta \cos 2\theta) - NM,$$

where  $H$  is the applied field at resonance and  $N$  is the demagnetizing factor in the plane of the disk-shaped sample.

Preliminary results with  $H$  parallel to the c-axis between 160° and 280°K show good agreement with the simple model described above, using an assumed g-value of 2.00 and  $K_1$  as determined by the torque measurements of Graham.<sup>(3)</sup> Figure 2 shows these results together with the predictions of Eq. (1) with and without anisotropy and demagnetizing corrections. The anisotropy and demagnetizing terms are of the same sign and of about equal magnitude. When  $H$  is parallel to the basal plane, the temperature dependence of the resonance results in a very complicated behavior indicating that higher order anisotropy terms may be important.

We determine from our data a splitting factor  $g = 2.0 \pm 0.1$  which value is consistent with Kip's earlier results<sup>(4)</sup> on polycrystalline samples and the results of Arajs and Colvin<sup>(5)</sup> from paramagnetic susceptibility. Our determination will be made more precise with better sample geometries, in particular by the use of single-crystal thin films that we are currently trying to prepare.

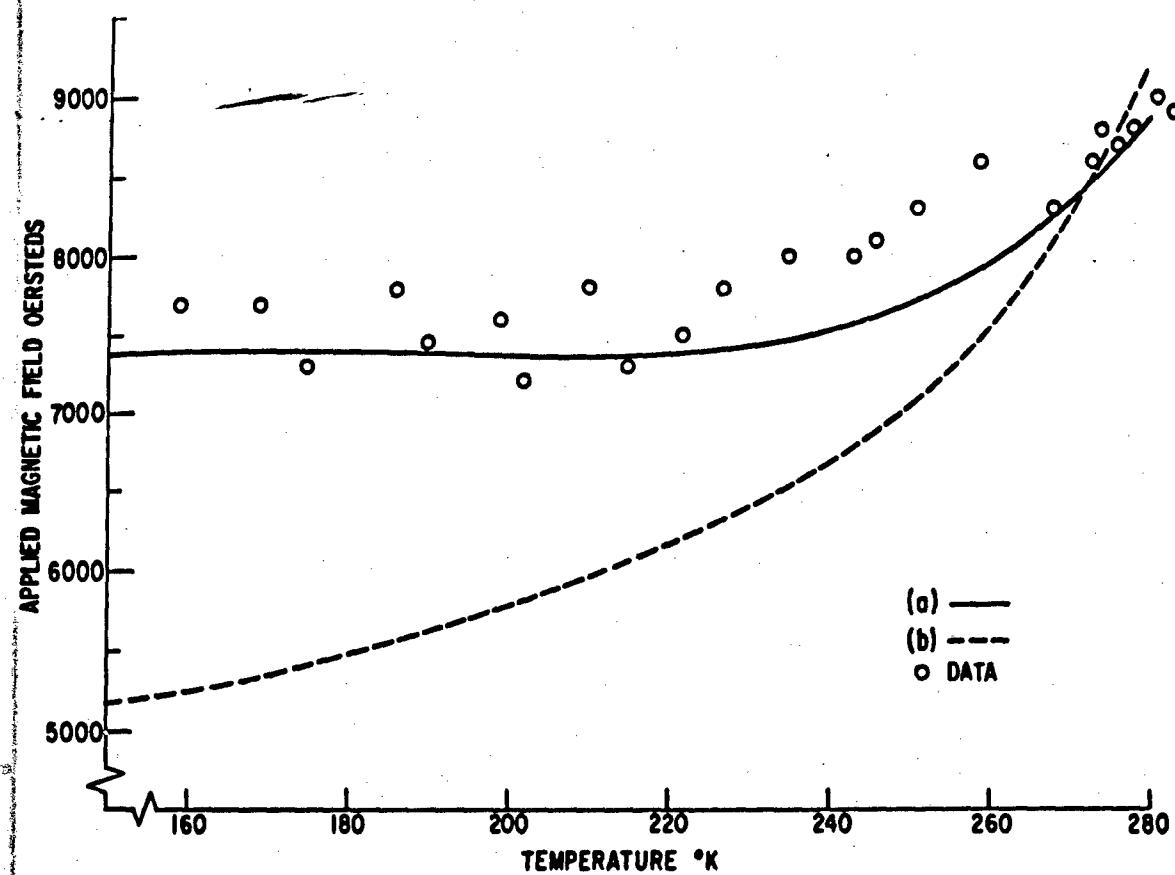


Fig. 2 The temperature dependence of the applied magnetic field required for resonance at 34 kMc/s. The crystal exposes a (1010) crystallographic plane to the microwave field. The applied d-c magnetic field is parallel to the <0001> direction; (a) is the plot of the Calculation indicated in the text with anisotropy and demagnetization accounted for; (b), is the effect of neglecting anisotropy and demagnetization within the plane of the sample. The data indicate the agreement with (a). The g factor is  $2.0 \pm 0.1$ .

Since in the transition metals we have come to expect a  $g = 2$ , perhaps it is worth a few words here to indicate the primary differences between the transition metals and the rare earths. The  $g = 2$  value for transition metals is a result connected with the phenomena of "quenching" of orbital angular momentum by the electrostatic field of the crystalline solid. The  $l$ - $s$  coupling usually operative for a free ion is not valid in the presence of large crystalline electric fields. The effect of these fields is essentially to remove the contribution of the orbital angular momentum. Thus, for transition metal ions with this "quenching" a  $g$  value characteristic of spin only ( $g = 2$ ) is obtained. In the rare earths, the  $f$  electrons lie deeply within the atomic core and do not interact strongly with the crystalline electric field.

For the rare-earth metals the free ion view of the Landé factor is essentially correct, i.e.,  $j$  is a good quantum number and we must determine it by the proper addition of  $l$  and  $s$ . We are then to expect, in general,  $g \neq 2$  for the rare earth elements. A special case is that of gadolinium which is a  $Gd^{3+}$  ion and is thus in the ionic state  $^8S_{7/2}$  and should have a  $g = 2$ .

Of further interest is the exchange interaction in the metal. Since the magnetic moment of the rare-earth metal comes from the 4 f electronic shell it is well shielded by outer electronic shells of the atom, (6) direct exchange interactions between 4 f electron shells is very small and it is necessary to examine other exchange mechanisms to account for the ferromagnetic Curie temperature. The most likely indirect exchange mechanism is that due to the conduction electron polarization. The quantitative application of this idea to the rare earths was first calculated by Kasuya, (7) DeGennes, (8) firmly established this to be the case as has the work of Bozorth et al. (9)

The current work is intended to extend the temperature range of the data and the accuracy of the analysis. Efforts to make thin-film single crystals have not yet proven successful.

We have prepared new single-crystal specimens for subsequent examination. From these experiments we hope to unambiguously describe the anisotropy constants and g-factor of gadolinium metal. The experiments are to be the resonance absorption at both 8 mm and 12 mm microwave radiation. The samples have quite good line widths--superior to our previous samples and thus we anticipate more precision. In addition, for the identical sample and its orientation, the resonance at two frequencies gives an unambiguous result for the anisotropy constants and the splitting factor,  $g$ , provided only that neither the magnetization nor the anisotropy is a strong function of the applied field. In this assumption we may indeed learn something as there is independent evidence that the anisotropy (10) as well as the magnetization (11) are field dependent. The latter evidence (i.e., magnetization) we are in the process of checking by studying the magnetization of a single crystal as a function of temperature in fields to 140 kOe.

## 2. Thermal Expansion Anomaly in Gadolinium and Nickel (DSB)

The observation (12) of negative thermal expansion in gadolinium and other rare-earth metals is indicative of the magnetic exchange interaction between atoms and its dependence upon atomic separation. In fact, the measurement by Patrick (13) of the coefficient of the pressure dependence of the Curie temperature for gadolinium allows us to calculate the expected thermal expansion. We employ the results of a recent study (14, 15) of the consequences of exchange interaction sensitivity to atomic separation and obtain the results quoted here and shown in Fig. 3. The magnetic contribution to thermal expansion is calculated from the theory mentioned as follows.

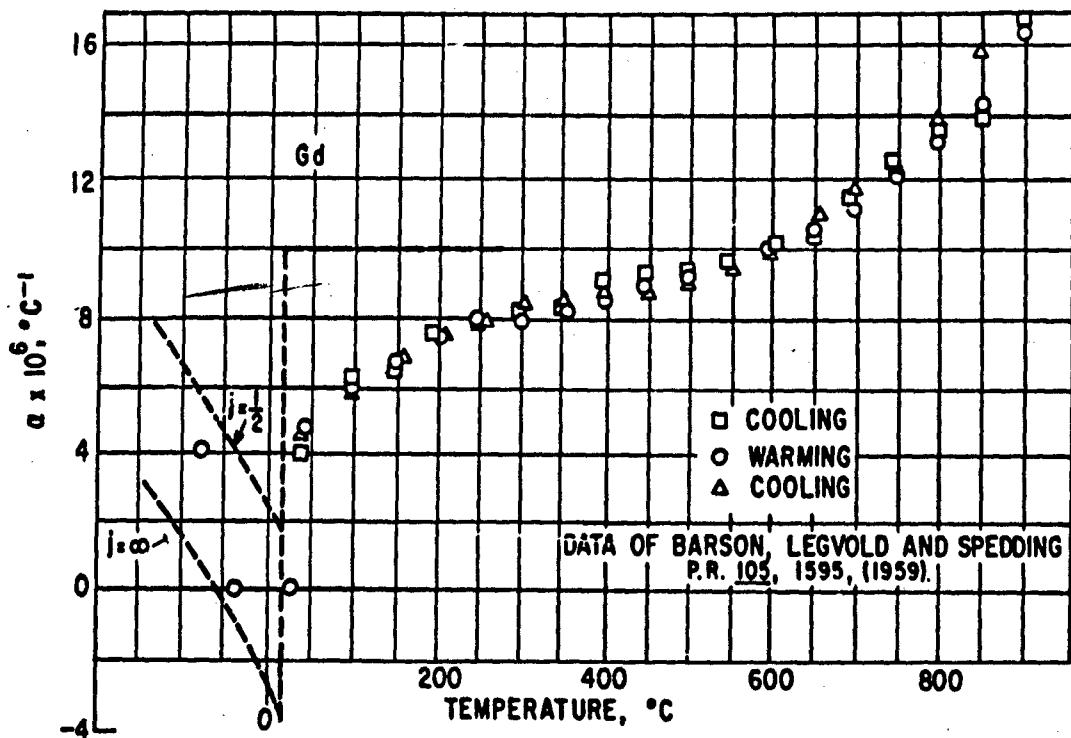


Fig. 3 The measurements of Barson, Legvold, and Spedding for the thermal expansion of polycrystalline gadolinium compared to the dependence calculated using (4) of the text. The evaluation is made for  $j = 1/2$  and  $j = \infty$  to show the range to be expected. The background lattice thermal expansion is taken as  $10 \times 10^{-6} / ^\circ\text{C}$  and assumed constant for the purposes of this evaluation.

From the treatment given in Refs. 14 and 15, we take the equilibrium spontaneous volume distortion of a magnetic lattice to be:

$$\frac{v-v_0}{v_0} = \frac{3}{2} \frac{1}{j+1} N K k T_0 \beta \sigma^2 - P K + \alpha_g T \quad (4)$$

In Eq. (4),  $v$  is the specific volume while  $v_0$  is the volume that would pertain at  $0^\circ\text{K}$  with neither magnetic interaction nor applied pressure.  $N$  is the number of magnetic ions per cubic centimeter of angular momentum  $j$  h,  $K$  is the compressibility,  $k$  the Boltzmann constant,  $T_0$  the Curie temperature when the volume is  $v_0$ , and  $\beta$  is the slope of the Curie temperature dependence on specific volume.  $\sigma$  is the spontaneous magnetization relative to its saturation value at  $0^\circ\text{K}$ .  $P$  is the pressure,  $\alpha_g$  is the lattice thermal expansion, and  $T$  the absolute temperature.

The derivative of (4) with respect to temperature is the total volume thermal expansion and is

$$\alpha_t = 3 \frac{j}{j+1} NkKT_0 \beta \sigma \frac{d\sigma}{dT} + \alpha_l . \quad (5)$$

A parameter that is of consequence in the magnetic behavior of materials as viewed in this framework is given below as

$$\eta = \frac{5}{2} \frac{[4j(j+1)]^2}{[(2j+1)^4 - 1]} NkKT_0 \beta^2 . \quad (6)$$

This parameter indicates whether or not one expects the over-all magnetization behavior to depart appreciably from that determined by the use of the Brillouin function which corresponds to  $\eta = 0$ . If  $\eta > 1$ , in fact, the transition to paramagnetism will be thermodynamically of first order. We evaluate this parameter here to determine whether  $\sigma$  vs  $T$  need to be calculated in modified form since we need  $\sigma$  ( $d\sigma/dT$ ) for use in (5). The evaluation of (6) indicates that  $\eta$  (gadolinium) = 0.019 and thus we do not expect a departure from the simple magnetization behavior usually calculated for  $j = 7/2$  appropriate to gadolinium. We have evaluated (5) using  $-1.2^\circ\text{C}/1000$  atmospheres<sup>(13)</sup> as the pressure dependence of the Curie temperature and with  $K = 2.5 \times 10^{-12} \text{ cm}^2/\text{dyne}$ <sup>(16)</sup> we have determined the magnetic contribution to thermal expansion. The results are displayed in Fig. 3 where we have chosen  $\alpha_l = 10 \times 10^{-6}/^\circ\text{C}$  as the linear lattice contribution taken as constant. Elsewhere in this report we make use of the integrated magnetic distortion which from (4) must correspond to the total distortion resulting when  $\sigma = 1$ , i. e.,

$$\int_0^\infty \alpha_{\text{mag}} dT = \frac{3}{2} \frac{j}{j+1} NkKT_0 \beta \text{ or } \frac{3}{2} \frac{j}{j+1} Nk \frac{dT_c}{dP} , \quad (7)$$

the latter expression coming from the definition of  $\beta$ . Application of this same approach to nickel and to  $\alpha\text{Fe}_2\text{O}_3$  (mentioned elsewhere in this report) have also been made and are in surprisingly good agreement considering the oversimplified view of the theoretical treatment. The neglect of short-range order above the Curie point is characteristic of the molecular field approach to magnetism and is a major source of discrepancy in the present treatment when one looks carefully at the behavior of  $\alpha$ ; however, the integrated behavior<sup>(7)</sup> is not as sensitive'y dependent on the details. This is analogous to specific heat anomaly and its relationship to the total magnetic entropy. We believe that the application of this simple physical picture provides an insight into many phenomena connected with magnetism.

For nickel the magnetic contribution is of opposite sign, i.e., positive for nickel, negative for gadolinium. The fact that the exchange interaction of magnetic atoms is dependent upon separation between atoms is a well-known and useful feature of magnetism despite the fact that "first principle" calculations of the dependence is prohibitively difficult in most cases. On the other hand, the existence of this separation-dependent interaction leads naturally to a distortion of a magnetic solid that depends on temperature because the magnetic order depends on temperature. This is, of course, the magnetic contribution to thermal expansion. It is possible to make a simple thermodynamic argument about the size of this effect that is both instructive and utilitarian, and that is what we have previously indicated with application to gadolinium. In Fig. 4 is shown the data of Nix and MacNair(17) of the thermal expansion coefficient of a polycrystalline nickel sample as a function of temperature. In their work they fit a lattice thermal expansion curve to their data using the Debye approximation with  $\theta_D = 410^\circ\text{K}$ . We have calculated the magnetic contribution in the spirit of the theory outlined above and have used Patrick's value of  $0.35^\circ\text{C}/10^3$  bars to be the pressure dependence of the Curie temperature of nickel. With this value, the material constants of nickel and the  $j = 1/2$  magnetization vs temperature we have calculated the lines shown in Fig. 4. The solid line is for  $\theta_D = 410^\circ\text{K}$ ; the dashed line for  $\theta_D = 450^\circ\text{K}$ . The lack of detailed agreement arises from two things.

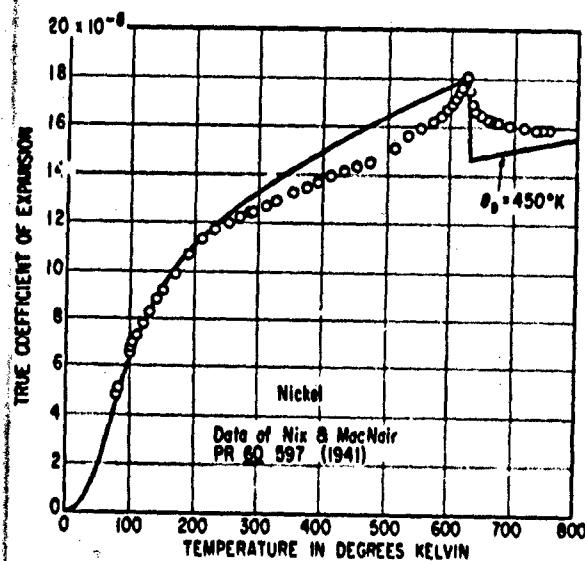


Fig. 4 The thermal expansion of nickel by Nix and MacNair compared to theory. The value of  $\theta_D = 410^\circ\text{K}$  was used by Nix and MacNair; we have added the magnetic contribution to the lattice term for that value of  $\theta_D$  as well as  $\theta_D = 450^\circ\text{K}$ .

Important is due to neglect of the short-range order above the Curie temperature and that, when included, will aid agreement above  $T_c$ . The general result for nickel is a satisfactory agreement between theory and experiment

in the sense that the proper magnitudes are accounted for from a simple and instructive theory. The same could be said for our previous calculation of thermal expansion of gadolinium; however, when one examines the data for iron it is difficult to account for that behavior using the same simple picture. Thus we are encouraged to examine further modifications of this approach as it seems a rewarding direction in which to move.

3. Nuclear Resonance of f.c.c. Cobalt Particles Precipitated in a Copper-Cobalt Alloy (DSR)

We have been interested in the possibility of determining coherency strains by the method of nuclear magnetic resonance. This possibility exists in the case of cobalt because of the large strain sensitivity associated with its nuclear resonance frequency. (18, 19)

In the system 3 per cent Co-balance Cu, it is possible to obtain a precipitated phase of cobalt-rich material coherent with the copper-rich lattice, but under a sizable lattice mismatch. We have adopted a high sensitivity superregenerative oscillating-detector to search for the frequency of nuclear resonance and to measure its dependence on precipitate particle size and temperature. We have been successful in finding the resonance in a nominally 50 Å (average radius) group of cobalt particles and are now processing new samples for the more detailed study that we shall report subsequently.

4. Magnetic Annealing in Cu-2 Per Cent Co Alloys (DSR)

We have recently performed and are currently analyzing the results of allowing the cobalt-rich precipitate particles in a Cu-2 per cent Co alloy to form under the presence of a large externally applied magnetic field. Our motivation derives from what appears to be a lack of detailed understanding as to how or if particles' shapes are affected by this treatment. The experiments we do are performed on well-defined single-crystal samples. In the measurement after heat treatment we rely on the ferromagnetic resonance absorption to give us primary information. An augmentative tool has been to examine the same samples under electron transmission microscopy through the kind cooperation of V. A. Phillips of this Laboratory.

5. Nuclear Resonance in MnAs (DSR)

A recent note in the Journal of the Physical Society of Japan (20) reported the observation of the nuclear resonance absorption in MnSb. The manganese compounds in this kind of structure (nickel arsenide type) are of interest to us, and in particular the homologous compound MnAs has been extensively examined in this Laboratory (outside the activities of this contract). The possibility of studying the local hyperfine fields by nuclear resonance in the MnAs material is very attractive. We have been able to observe the nuclear resonance in the compound MnAs. The experiment uses a powdered sample (wax coated) loading a coaxial transmission line. The variation in transmission of a frequency swept input signal reveals the resonance absorption of the sample nuclei. We observe both the Mn and As nuclei. An oscilloscope trace photograph of these resonance absorptions at 77°K for MnAs is reproduced

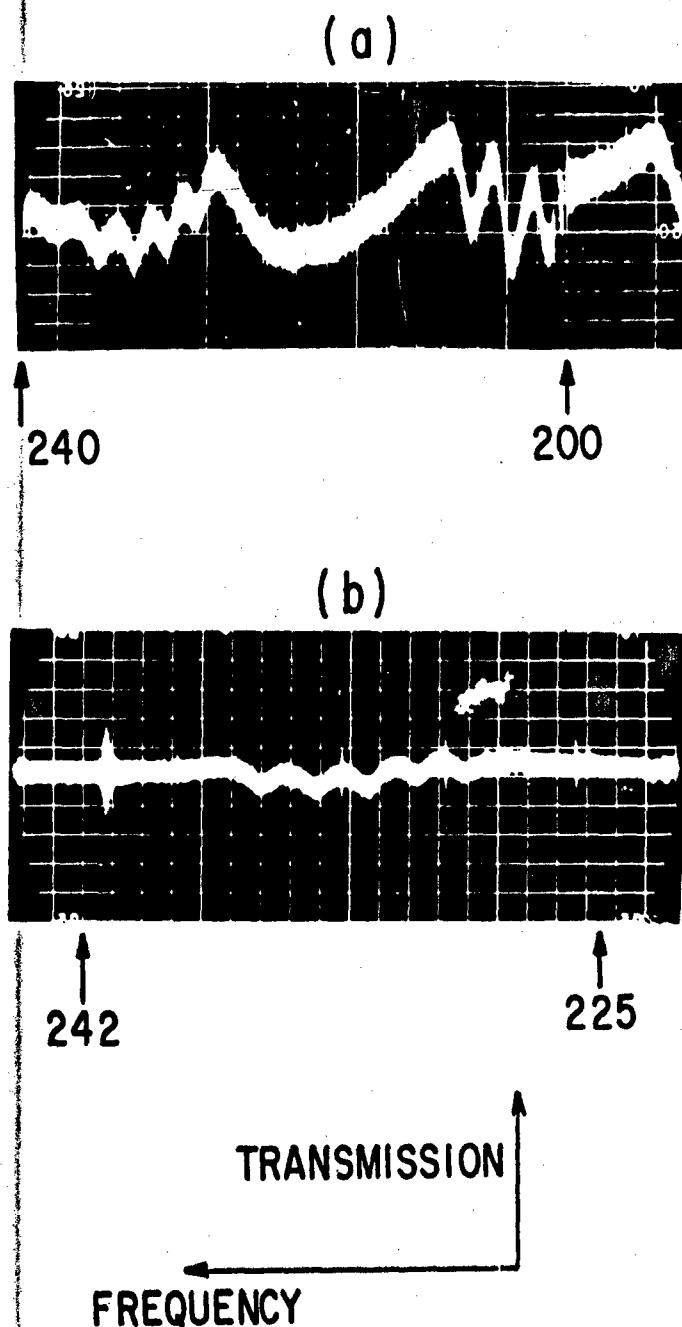


Fig. 5 Nuclear resonance absorption of MnAs and MnSb at 77°K: (a) MnAs showing absorption due to both Mn<sup>65</sup> and As<sup>75</sup>; (b) MnSb showing absorption due to Mn<sup>65</sup>. The frequency is given in Mc/s.

in Fig. 5. The Mn<sup>65</sup> has  $I = 5/2$  giving rise to a quintuplet of absorptions, the As<sup>75</sup> has  $I = 3/2$  giving rise to a triplet. The frequency scale is indicated below the oscilloscope trace. We have made no effort to achieve high-precision frequency measures as it appears that Hihara, Kōi, and Tsujimura(21) have already carefully documented these resonances. There are two very important features that appear in light of this work. These are as follows:

(a) The hyperfine field is presumed to arise from the s-d polarization by the magnetic Mn atoms. In all previous cases (Fe, Ni, Co) the sign of the net field was minus (i.e., opposite to the magnetization) while in the compounds above the field appears to be positive.

(b) The magnitude of the hyperfine field is smaller at the Mn atom nucleus than at the anion nucleus; a remarkable feature is as much as the Mn is the primary source of the polarization. It may be that the fact that the net hyperfine field is made up of large terms of opposite sign that causes this. For example, the conduction electrons and the bound s-like electrons both contribute large terms to the net field, usually of opposite sign, the absence of s-core

polarization of the anion because of its lack of unbalanced d-electrons would remove a large term of opposite sign to the conduction electrons and thus give a larger net field at the anion nucleus than at the Mn. It will be profitable to pursue these features in future work.

#### 6. Electron Tunneling into Ferromagnetic Metals (DSR)

Work in this Laboratory(22) has shown that it is experimentally possible to accomplish quantum mechanical "tunneling" through a thin insulating barrier that separates two metals. Furthermore, the voltage-current characteristic of such a "tunnel-junction" is sensitive to the electronic properties of the metals on both sides(23) of the junction. These features appear promising for this technique to be a useful tool in the study of electronic properties such as band structure and/or density of states of the conductors involved. In particular, since our interest is in ferromagnetic materials we have begun a series of experiments on tunneling between aluminum-aluminum oxide-ferromagnetic sandwiches prepared by sequential evaporation, oxidation, and evaporation. The ferromagnetic component consists of Ni-Cu alloys of various compositions between pure nickel and pure copper and Pd-Ag alloys between pure palladium and pure silver. The experiments measure the voltage vs current characteristic through the insulating aluminum oxide junction and the departures from linearity of these characteristics. There are several reasons for departures from linearity, but most of these lead to departures in directions opposite to those that are observed. We have chosen the alloys mentioned as it seems most reasonable that if band-structure effects are to be observed they will be observable in these alloys. Simultaneous with our interest in these experiments and external to this contract, H. R. Phillip at this Laboratory has undertaken a detailed examination of the optical properties of these alloys as the energy of visible and near visible quanta closely corresponds to band splittings in these alloys. We hope to complement each other's experimental findings and to rely upon the strong theoretical interest of H. Ehrenreich and W. A. Harrison also of this Laboratory for assistance in interpretation of the results. At the present time our tunneling experiments have revealed new behavior that we shall try to understand through subsequent work

#### 7. Thermal Expansion and the Néel Temperature of Antiferromagnetic $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (ISJ)

The mineral hematite which can be synthesized in the laboratory as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has frequently been the subject of study since the earliest years of research in magnetic compounds. One feature of this interest has centered on its weak ferromagnetism which is superposed on a more or less field-independent magnetic susceptibility. The weak ferromagnetism disappears at high temperature, about 675°C (varying slightly with sample purity and preparation) and also disappears or drops noticeably at low temperatures (around -20°C). Both of these transitions appear in the work of Honda and Sone,(24) and have been documented as well as rediscovered by many subsequent investigators. After various modifications, the presently accepted view is that the compound is predominantly antiferromagnetic at all temperatures

below 675°C; that the weak ferromagnetism is an intrinsic property of the bulk material arising mainly from a slight canting of the two antiferromagnetic spin sublattices toward each other owing to an anisotropic exchange mechanism proposed by Dzialoshinskii<sup>(25)</sup> on thermodynamic and symmetry reasoning and evaluated quantum mechanically by Moriya;<sup>(26)</sup> and that the low-temperature transition is associated with a change in magnetic symmetry owing to a rotation of the spin direction from the basal plane of the hexagonal unit cell to the c-axis thereof.<sup>(27)</sup> (The crystal structure is truly rhombohedral, but may also be considered as hexagonal without any sacrifice of rigor, and with some gain in mathematical simplicity.)

Recently, a suggestion has been made<sup>(28)</sup> that the high temperature at which the weak ferromagnetism vanishes (675°C) is not the antiferromagnetic Néel point, but that antiferromagnetic ordering persists until about 725°C. The evidence for this suggestion rests on differential thermal analysis data, and also on measurements of the internal field using the Mössbauer effect. Preliminary values from the latter technique gave ~725°C, but later were corrected to yield 690° ± 5°C.<sup>(29)</sup>

Inasmuch as the available neutron diffraction data through the high-temperature transition suffered from poor resolution and problems associated with short-range magnetic order and critical scattering phenomena, characteristic of the instrumental limitations of the pioneering work in this field, it was thought desirable to explore other "nonmagnetic" methods of ascertaining the Néel point. The thermal expansion effects associated with magnetic ordering seemed appropriate in view of the success of this approach with various antiferromagnetic monoxides,<sup>(30)</sup> and with regard for its lack of dependence on the weak ferromagnetism *per se*. At the time we were unaware of several earlier investigations of the thermal expansion of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Despite the redundancy of the present experiments, a correlation between the thermal expansion anomaly and the recent thermodynamic theory of magnetic transitions by Bean and Rodbell, (14, 15) discussed elsewhere in this report (Section 2) enables one to estimate the dependence of the Néel temperature on hydrostatic pressure. Alternatively, using existing data on the pressure dependence of the Curie temperature for related moment-bearing compounds, it is possible to identify the thermal expansion anomaly in a way roughly similar to the usual thermodynamic treatments of the anomalous specific heat of magnetic compounds.

Two methods of measurement were chosen. Dilatometric measurements were performed using a commercial Chevenard dilatometer, with the cooperation of R. F. Berning and R. L. Cook. The sample was a polycrystalline bar, sintered to about 85 per cent of theoretical density in an oxygen atmosphere at 1350°C for several hours. X-ray examination of the surface of this bar revealed no peaks other than those of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Two runs were carried out: the first (I) at a heating rate of 5°C/min between room temperature and 1000°C; the second (II) at the same heating rate, except that the rate was reduced to 1°C/min between 550° and 750°C, and a separate thermocouple monitored the temperature at the center of the 2.5-inch-long bar.

The recorder plots a continuous trace of  $\Delta l/l_0$  vs T compared with that of  $\Delta l/l_0$  are measured at various values of temperature. These may be converted to differential linear expansion coefficients  $(1/l)(dl/dT)$ . Abrupt changes in length or in the slope of the  $\Delta l$  curve are located by direct examination of the recorder trace. The linear expansion coefficients from the two runs are plotted in Fig. 6. As noted, a distinct break in the slope of the expansion curve ( $\Delta l$  vs T) was observed at  $690^\circ\text{C}$ . No evidence of a double transition, or of a higher temperature transition was observed.

A corroborative but less extensive measurement of the thermal expansion was carried out by x-rays with the cooperation of L. M. Osika and E. Lifshin. Powder patterns were recorded on film using  $\text{CoK}\alpha$  radiation at  $15^\circ$ ,  $650^\circ$ , and  $750^\circ\text{C}$ . Measurements on the  $(4, 1, \cdot 0)$  and  $(3, 1, \cdot 10)$  reflections were used to determine  $a_0$  and  $c_0$  for the hexagonal lattice. Values for the average (rather than differential) expansion coefficients are calculated, and their polycrystalline averages  $\bar{\alpha}_p = (\bar{\alpha}_c + 2\bar{\alpha}_a)/3$  are tabulated below along with the comparable values from the dilatometer experiment. See Table II.

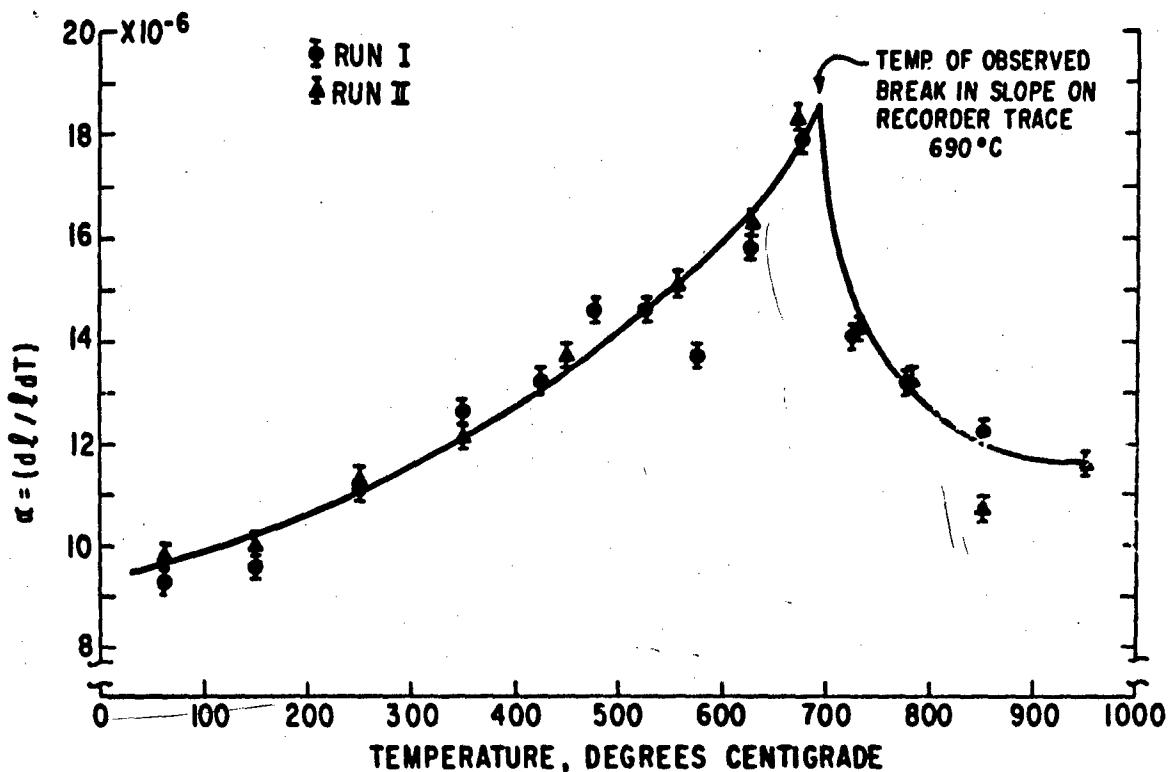


Fig. 6 Thermal expansion of polycrystalline, sintered bar of  $\alpha\text{-Fe}_2\text{O}_3$  (hematite).

TABLE II

$T_f - T_i$	Average Thermal Expansion Coefficients		$\bar{\alpha}_p \times 10^{+6}$	$\bar{\alpha}_p \times 10^{+6}$
	$\bar{\alpha}_a \times 10^{+6}$	$\bar{\alpha}_c \times 10^{+6}$		
$635^\circ - 15^\circ$	13.2	11.6	12.7	$12.3 \pm 0.3$
$751^\circ - 15^\circ$	13.9	10.8	12.8	$12.8 \pm 0.3$

Agreement between the two methods of measurement is very satisfactory.

In view of the prior work in this area, further experiments were unnecessary. Chaudron and Forestier<sup>(31)</sup> reported a similar dilatometric measurement which indicated a peak in the differential expansion coefficient at  $680^\circ\text{C}$ . Willis and Rooksby<sup>(32)</sup> carried out an extensive x-ray examination, plotting  $\alpha_a(T)$  and  $\alpha_c(T)$ .  $\alpha_a(T)$  exhibits a peak around  $670^\circ$  to  $680^\circ\text{C}$ , while  $\alpha_c(T)$  shows an abrupt, almost discontinuous rise centered around  $670^\circ$  to  $680^\circ\text{C}$  and confined between  $650^\circ$  and  $710^\circ\text{C}$ . These results strongly support the view that the temperature at which the weak ferromagnetism is reported to disappear is identical with the breakdown of antiferromagnetic ordering.

A correlation between the observed thermal expansion anomaly and the thermodynamic theory of this quantity is of interest. As shown elsewhere in this report, the formulation of Bean and Rodbell may be used to express the magnetic contribution to the volume thermal expansion:

$$\alpha_{\text{vol., mag.}} = 3\alpha_{p, \text{ mag.}} = \frac{3j}{j+1} NkT_0 \beta \sigma \frac{d\sigma}{dT} . \quad (8)$$

Here  $j$  is the magnetic quantum number,  $N$  is the number of magnetic atoms per cc,  $k$  is Boltzmann's constant,  $K$  is the compressibility,  $T_0$  is the magnetic ordering temperature of the equivalent incompressible lattice,  $\beta$  is the slope of the dependence of  $T_c$  (the actual magnetic ordering temperature) on volume, and  $\sigma$  is the relative (sublattice) magnetization. From the defining equation for  $\beta$  and  $T_0$ , one has  $\beta T_0 K = -dT_c/dP$ . Thus:

$$\alpha_{\text{vol., mag.}} = - \frac{3j}{3+1} Nk \frac{dT_c}{dP} \sigma \frac{d\sigma}{dT} . \quad (9)$$

If we are interested only in the total excess thermal expansion associated with the transition from magnetic order to disorder, we obtain

$$\int_0^\infty \alpha_{\text{vol.}, \text{mag.}} dT = - \frac{3jNk}{j+1} \frac{dT_c}{dP} \int_1^0 \sigma d\sigma \quad (10)$$

$$= \frac{3jNk}{2(j+1)} \frac{dT_c}{dP} \quad (11)$$

This expression could have been obtained more directly, but the intermediate relations are also of interest. Evaluated for  $\alpha\text{-Fe}_2\text{O}_3$ , with  $j = 5/2$ , Eq. (11) yields

$$\int_0^\infty \alpha_{\text{vol.}, \text{mag.}} dT = 5.9 \times 10^{+6} (dT_c/dP) \quad (12)$$

On the experimental side, integration of the area in Fig. 6 between 50° and 950°C, closed crudely by a straight line connection those two extreme data points gives a value

$$\int \alpha_p, \text{mag.} dT = 2.05 \times 10^{-3} \quad (13)$$

or since  $\alpha_v = 3 d\ell/\ell dT$ , we have

$$\int \alpha_{\text{vol.}, \text{mag.}} dT \approx 6 \times 10^{-3} \quad (14)$$

Comparison with the theory suggests a value for  $dT_c/dP \approx +1 \times 10^{-9}$ , or about 1°C/kilobar.

The estimate for  $dT_c/dP$  is based on an isotropic theoretical model and one should not be surprised to find deviation from it, especially in view of the anisotropic thermal expansion near the Néel point. The "isotropic" estimate would also be affected by any anisotropy in the linear compressibility. Such data are not available for  $\alpha\text{-Fe}_2\text{O}_3$ , but measurements have been reported by Bridgman(33) on the isomorphous compound  $\text{Al}_2\text{O}_3$ . Somewhat surprisingly, there is little if any difference between the linear compressibilities measured perpendicular to the c-axis (of the hexagonal cell), and nearly parallel thereto. The same conclusion is obtained from the values of the elastic constants for  $\alpha\text{-Fe}_2\text{O}_3$ . (34)

A possible experimental approach to evaluating  $dT_c/dP$  is through the study of nuclear magnetic resonance in  $Fe_2O_3$ . The internal hyperfine fields would change greatly with temperature near the Néel point, and in turn be sensitive to hydrostatic pressure. Room temperature, atmospheric pressure nmr experiments on related iron oxides have been reported.(35)

Lastly, one may compare the prediction of  $dT_c/dP$  with measurements on related moment-bearing compounds. In the research of Patrick,(13) two compounds were examined whose magnetic exchange is largely due to superexchange through an intervening oxygen anion. These are the ferromagnetic perovskite (double-exchange and super-exchange)  $La_{0.75} Sr_{0.25} MnO_3$ , whose Curie point is about  $80^\circ C$ , which  $dT_c/dP = +0.6^\circ C/kb$ ; and the ferrimagnetic spinel  $Mn_{0.5} Zn_{0.5} Fe_2O_4$ , whose Curie point is near  $90^\circ C$ , for which  $dT_c/dP = +0.9^\circ C/kb$ . In the former compound the electronic states of the magnetic ions ( $Mn^{3+}$ ,  $d^4$ ;  $Mn^{4+}$   $d^3$ ) differ from those in  $\alpha-Fe_2O_3(Fe^{3+}, d^5)$  while the immediate crystallographic environment is similar (octahedral). In the latter compound these roles are reversed: the electronic states are similar, while part of the crystallographic environment is different. In spite of these precautionary remarks, the similarity between the predicted  $dT_c/dP$  and those observed is striking. The conclusion one may draw, apart from that of some rough validity of the predicted  $dT_c/dP$ , is that the recent formulation of the theory of magnetic materials puts our understanding of thermal expansion in magnetic materials on a firmer basis and converts thermal expansion data into a research tool of wider applicability.

Since this work was performed, another determination of the thermal expansion has been reported, also stimulated by the report of Aharoni *et al.*(28) In this work Robbrecht and Doclo(36) detected double peaks in the thermal expansion of hematite at both the low temperature transition region ( $-40^\circ$ ,  $-10^\circ C$ ) and the Néel point region ( $680^\circ$ ,  $725^\circ C$ ). The previous measurements above room temperature cited herein had not seen double peaks. The differential thermal analysis work of Aharoni *et al.*(28) had seen two transitions near the Néel point, ( $675^\circ$ ,  $725^\circ C$ ) but only one in the low-temperature region ( $-30^\circ C$ ). This may be viewed as possible support, but not for the interpretations offered, in view of the revised Mössbauer determination of the Néel point.(29) Alternatively, one may question the subsidiary thermal expansion peaks. If one were to redraw smoothed curves through the data points of the "subsidiary transitions" without slope discontinuities, the points ignored in so doing would not deviate from the smoothed curve any more than do some points ignored by the smoothed curves constructed by these investigators.

#### 8. Antiferromagnetic Behavior of $FeCO_3$ (ISJ)

This study was initially undertaken during the latter part of the previous contract term, and progress was summarized in ASD Technical Report No. 61-630. During the current period, work on this problem was resumed. Previous work on  $FeCO_3$  is as follows: Foëx(37) investigated the highly anisotropic susceptibility in the paramagnetic range on a natural mineral crystal (siderite); Becquerel(38) studied the Faraday rotation above

and below the magnetic ordering temperature on two mineral samples, suggesting ordering temperatures near 60°K for one and near 35°K for the other; Bizette<sup>(39)</sup> studied the susceptibility as a function of temperature down to 14°K on a natural crystal with a Néel temperature near 35°K and on synthesized powder with a Néel temperature near 57°K; Alikhanov<sup>(40)</sup> recently examined the magnetic structure by neutron diffraction on a mineral sample finding a Néel point at 35°K, with the atomic moments aligned anti-ferromagnetically parallel to the c-axis (trigonal symmetry) of the rhombohedral calcite structure; and Pickart<sup>(41)</sup> also studied the magnetic structure by neutron diffraction, inferring a Néel temperature near 20°K, but finding the same structure as did Alikhanov. From the specific results obtained in neutron diffraction, as well as from inferences following the works of Becquerel and Bizette, one would identify  $\text{FeCO}_3$  as a likely choice for the occurrence of an abrupt magnetic transition, in contrast to  $\text{MnCO}_3$  and  $\text{CoCO}_3$  whose magnetic moments lie antiparallel, in the basal plane of the calcite structure.

The initial work was done on powder and nearly monocrystalline specimens obtained from natural siderite samples found at Roxbury, Connecticut, and purchased through Ward's Natural Science Establishment, Rochester, New York. Chemical analysis and x-ray diffraction have revealed a second phase impurity (about 3 per cent by weight) in the form of  $\text{SiO}_2$  (quartz), and some solid solution impurities of  $\text{MnCO}_3$  and alkaline earth carbonates (Ni, Co, and Zn were not detected). An approximate formula is  $(\text{Fe}_{0.83} \text{Mn}_{0.05} \text{R}_{0.12}) \text{CO}_3$ , where R is Mg and/or Ca, Sr, or Ba. During this contract period better oriented crystals were obtained from siderite chunks. The monocrystalline nature and the orientation of the crystals selected were checked by x-rays with the cooperation of W. L. Roth, L. M. Osika, and E. Lifshin. Faces perpendicular and parallel to the trigonal axis (c-axis) were ground with accurate orientation by E. Stella using the combination x-ray orientation and grinding unit designed by E. H. Jacobsen. The magnetization of these crystals, as well as of siderite powder, was measured to 200 kOe, at 4.2° and 77°K, extending the earlier measurements by about 55 kOe. The susceptibility curves (at 10 kOe) as a function of temperature between 4.2° and 300°K on both crystals and powder were obtained with the cooperation of C. C. Hartelius and J. S. Kovel.

The initial indications reported under the previous contract term were carried to a sufficiently informative stage that a paper covering this work was presented at the Eighth Annual Conference on Magnetism and Magnetic Materials, held in Pittsburgh, Pennsylvania, November 12-15, 1962. The text of that paper will be published in the Conference Proceedings, a Supplement to the Journal of Applied Physics, in March 1963. It appears below, followed by additional comments and plans for future work.

## METAMAGNETISM OF SIDERITE ( $\text{FeCO}_3$ )

I. S. Jacobs  
General Electric Research Laboratory  
Schenectady, New York

A uniaxial antiferromagnet with high anisotropy should show a sharp transition to a ferromagnetic configuration in fields sufficient to overcome the antiferromagnetic exchange. Examples of this restricted type of metamagnetism are rare, but are here extended to ferrous carbonate in its natural mineral form, siderite. Magnetic susceptibility measurements on powder and oriented crystals at 10 kOe between  $4.2^\circ\text{K}$  and  $300^\circ\text{K}$  confirm in detail the high anisotropy and indicate a Néel point at  $38^\circ\text{K}$  for this mineral. Pulsed field magnetization measurements to 200 kOe at  $4.2^\circ\text{K}$  exhibit a metamagnetic transition toward ferromagnetism starting near 100 kOe for both the powder and c-axis oriented crystal. The transition in this crystal is nearly complete at 200 kOe where the magnetization approaches a saturation of about  $6\mu\text{B}$  per iron ion. From an elementary statistical model of the broad transition, the critical field for pure  $\text{FeCO}_3$  is estimated at about 200 kOe. These data and other factors lead to a conclusion that the predominant exchange interaction in  $\text{FeCO}_3$  is antiferromagnetic.

---

Néel<sup>(42)</sup> has described how the magnetization processes in uniaxial antiferromagnets reveal their anisotropy and exchange energies. With an intermediate anisotropy value the magnetization exhibits spin-flopping, while for larger anisotropy a sharp transition, termed metamagnetic, to a ferromagnetic configuration is expected. This restricted type of metamagnetism is rare, occurring in ferrous chloride<sup>(43, 44)</sup> and possibly in cobaltous sulfate.<sup>(45)</sup> Other sharp field-induced transitions from antiferromagnetic to ferromagnetic states either start from a helical configuration or exhibit first order transitions between such states at zero field.

Ferrous carbonate, occurring naturally as the mineral siderite, has a rhombohedral (calcite) structure. Magnetic susceptibility<sup>(37, 39)</sup> optical rotation, <sup>(38)</sup> and neutron diffraction<sup>(40, 41)</sup> measurements have established antiferromagnetic behavior (Néel points,  $T_N$ , ranging between  $20^\circ$  and  $60^\circ\text{K}$ ) with the  $\text{Fe}^{2+}$  moments pointing along the trigonal (c) axis, in alternating (0001) ferromagnetic sheets. Both paramagnetic and antiferromagnetic states are strongly anisotropic. Kanamori<sup>(46)</sup> investigated the crystalline field origin of the  $\text{Fe}^{2+}$  anisotropy in  $\text{FeCl}_3$  and noted its applicability to the carbonate structure.

He concluded that an Ising model is a good low-temperature approximation, with moments tightly bound to the c-axis. Thus  $\text{FeCO}_3$  should show a metamagnetic transition.

Magnetization measurements to 10 kOe at temperatures between  $4.2^\circ$  and  $300^\circ\text{K}$ , and in pulsed fields(47) to 200 kOe at  $4.2^\circ$  and  $77^\circ\text{K}$  were taken on siderite samples from Roxbury, Connecticut. Irregularly shaped adjacent monocrystalline pieces were oriented for measurements with the field parallel ( $\parallel$ ) or perpendicular ( $\perp$ ) to the c-axis. A cylindrical powder sample (P) was formed enabling absolute measurements. The magnetization scales for the crystals were fixed by invoking the susceptibility relation  $\chi_P = (\chi_{\parallel} + 2\chi_{\perp})/3$  at  $4.2^\circ$  and  $77^\circ\text{K}$ . With this determination the relation was confirmed within  $\pm 3$  per cent of all temperatures measured. Chemical and x-ray diffraction analysis revealed a 3 per cent  $\text{SiO}_2$  impurity, for which all data were corrected. The remaining carbonate composition was  $(\text{Fe}_{0.83} \text{Mn}_{0.05} \text{R}_{0.12})\text{CO}_3$  where R is an alkaline earth. The range of previous  $T_N$  values is ascribable to varied compositions which have not always been documented.

The magnetic susceptibilities derived from measurements to 10 kOe are presented in Fig. 7 for the three samples. The peaks in  $\chi_{\parallel}$  and  $\chi_P$  indicate a Néel point at  $\sim 38^\circ\text{K}$ , similar to some other mineral samples. (38-40) The parallel susceptibilities above  $T_N$  agree with data of Foëx, (37) but the perpendicular values are smaller by one-half. The anisotropy in susceptibility is very large with  $(\chi_{\parallel}/\chi_{\perp})$  reaching 8.8 at  $T_N$ .

The high field curves for these samples are presented in Fig. 8, including a scale of Bohr magnetons ( $\mu_B$ ) per magnetic cation (Fe, Mn) whose absolute magnitude has an uncertainty of  $\pm 4$  per cent arising in the calibration procedures and chemical analyses. The transition toward ferromagnetism occurs with both the  $\sigma_{\parallel}$  and  $\sigma_P$  curves, starting at about 100 kOe in each. The  $\sigma_{\parallel}$  transition appears nearly complete at 200 kOe, where it approaches a ferromagnetic saturation of about  $6\mu_B$  per ferrous ion. The much broader powder transition is expected with an Ising-like model.(47)

Ideally the  $\sigma_{\parallel}$  transition should be restricted to a narrow field range. The identification of the transition process is substantiated by the observation that both the  $\sigma_{\parallel}$  and  $\sigma_P$  transitions start at closely the same field. This feature precludes an association with the spin-flop process.(42, 48) Theories of the metamagnetic transition(42, 46, 49) set the critical field proportional to the anti-ferromagnetic interaction. To fix this value for  $\text{FeCO}_3$  from the siderite observations, a model is invoked ascribing the broad transition to a spread in effective antiferromagnetic interactions owing to the random distribution of nonmagnetic cations. The critical field

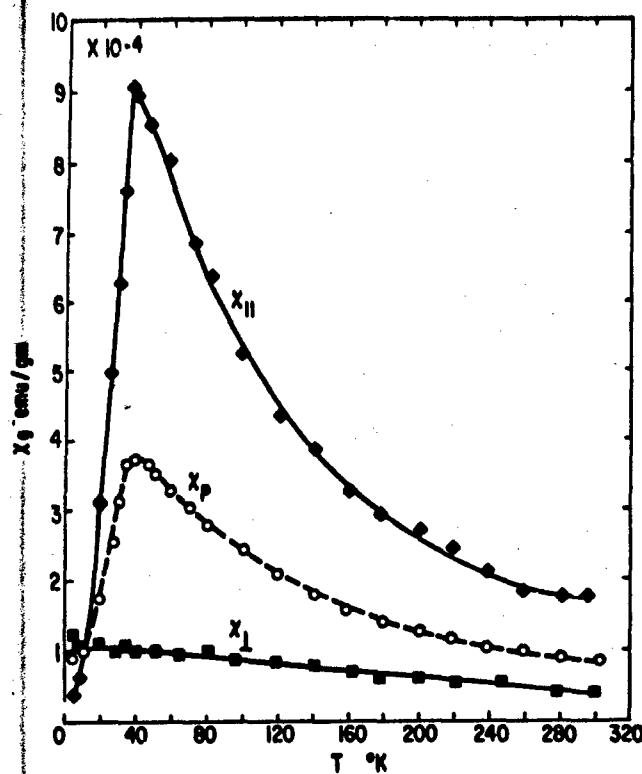
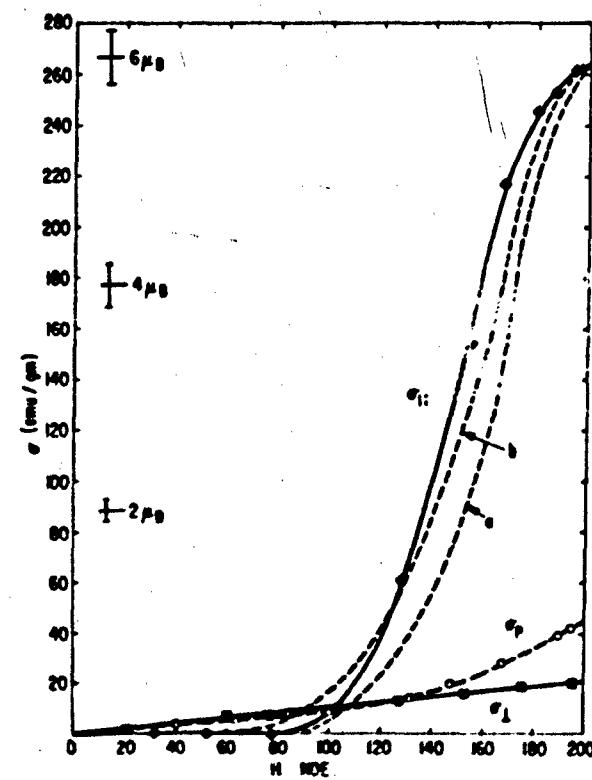


Fig. 7 Magnetic susceptibility at 10 kOe of Roxbury siderite vs temperature. Data for a powder (P) and with the field parallel (II) and perpendicular (L) to the c-axis of monocrystals.

Fig. 8 Magnetization curves at 4.2°K for the samples of Fig. 1, also indicating Bohr magnetons ( $\mu_B$ ) per magnetic cation. Curves (a) and (b) calculated as described in text.



for a given ferrous ion is assumed proportional to the number of nearest neighbor cations which are magnetic. Smoothed transition curves (a) and (b) are plotted in Fig. 8 for nonmagnetic cation concentrations ( $y$ ) of 0.12 and 0.17, respectively, normalized to a saturation of  $6\mu B$  and a critical field of 200 kOe for  $y = 0$ . The lower and higher  $y$  values, respectively, equate the manganese behavior with the iron or the alkaline earths. The fair agreement supports the model and the estimate that the critical field for pure  $\text{FeCO}_3$  is about 200 kOe.

This model neglects ferromagnetic intraplane interactions which analyses have shown to be dominant in  $\text{FeCl}_2$ . Justification is found by inspection of possible superexchange paths in the two compounds. Letting  $X$  be  $\text{Cl}^-$  or  $\text{O}^{2-}$  as appropriate and neglecting path angles, one associates the strong interaction  $\text{Fe}-X-\text{Fe}$  with ferromagnetic coupling in  $\text{FeCl}_2$  and antiferromagnetic in  $\text{FeCO}_3$ . Similarly, the weak interaction  $\text{Fe}-X-X-\text{Fe}$  corresponds to anti-ferromagnetic coupling in  $\text{FeCl}_2$  and ferromagnetic coupling in  $\text{FeCO}_3$ . Further evidence comes from applying these results to existing analyses<sup>(46, 49)</sup> thus obtaining negligible (if positive at all) ferromagnetic interaction in  $\text{FeCO}_3$ .

The author acknowledges discussions with J. S. Kouvel and extensive experimental help from P. E. Lawrence and C. C. Hartelius.

To assist in visualizing some of the points made in the preceding short paper (whose size was rigidly limited), two additional figures are presented herein. In Fig. 9, a comparison of the monocrystalline and polycrystalline behavior is presented for two kinds of magnetization processes in uniaxial antiferromagnets. This comparison supports the identification of the transition observed in siderite as a metamagnetic  $\text{AF} \rightarrow \text{F}$  process.

A schematic comparison of possible superexchange paths in  $\text{FeCl}_2$  and  $\text{FeCO}_3$  is presented in Fig. 10. For each structure, the alternating ferromagnetic cation layers, perpendicular to the c-axis, are shown along with the anions ( $\text{Cl}^-$  or  $\text{O}^{2-}$ ) believed to participate in the superexchange. The possible interactions of a particular  $\text{Fe}^{2+}$  ionic moment with its neighbors are indicated by a heavy solid or a heavy dashed line. As indicated on the figure, the heavy solid lines show exchange through a single anion, believed to be relatively strong and accounting for a ferromagnetic coupling in  $\text{FeCl}_2$  but for an antiferromagnetic one in  $\text{FeCO}_3$ . The dashed lines point to possible exchange through two anions, probably weak, and corresponding to anti-ferromagnetic coupling in  $\text{FeCl}_2$  but ferromagnetic in  $\text{FeCO}_3$ . The contrasting strengths of the antiferromagnetic coupling in the two compounds are completely in accord with the values of their transition fields, i.e.,  $\sim 10$  kOe for  $\text{FeCl}_2$  and  $\sim 100$  to 200 kOe for  $\text{FeCO}_3$ .

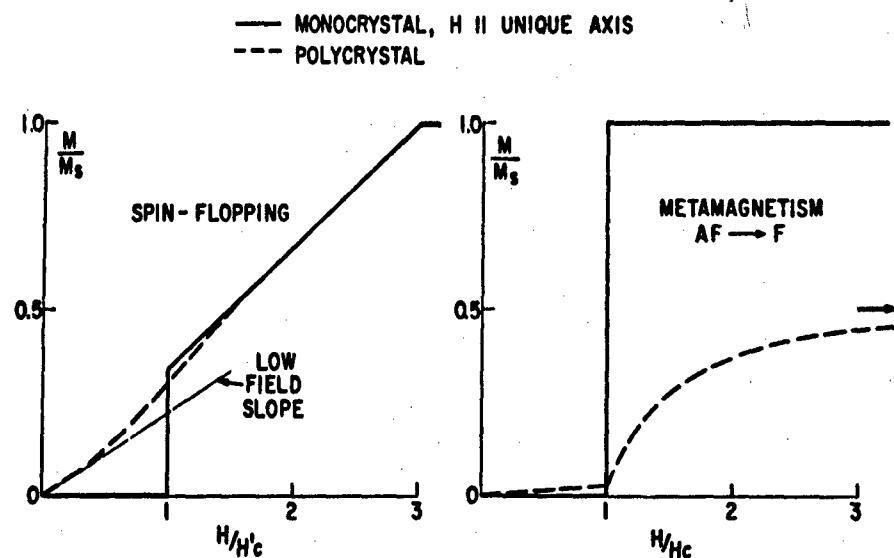


Fig. 9 Comparison of monocrystalline vs polycrystalline magnetization curves in uniaxial antiferromagnets.

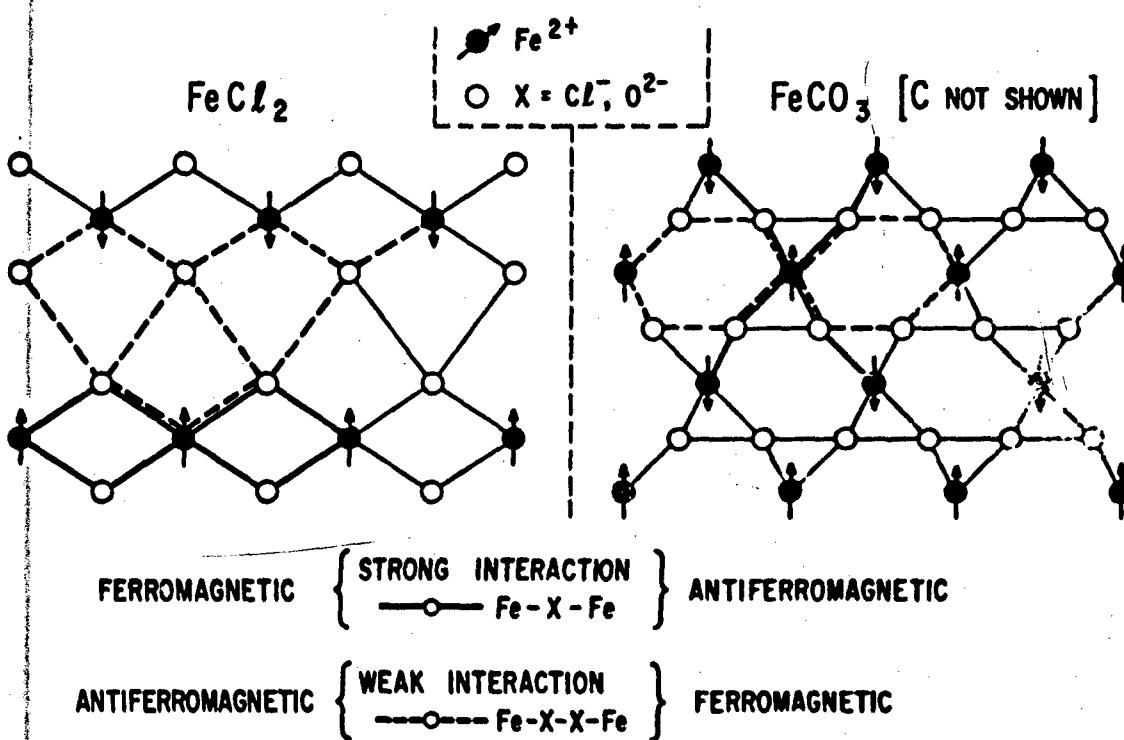


Fig. 10 Schematic comparison of possible superexchange paths.

As noted in Progress Report No. 2, certain unresolved problems might be tested by measurements on  $\text{FeCO}_3$  of higher purity than obtainable in the siderite mineral specimen. During this contract period, some 10 grams of synthesized powder was purchased from Tem-Pres Research, Inc., State College, Pa. Initial experiments carried out have presented both encouraging and discouraging aspects. Measurement of the high field magnetization to 200 kOe at  $4.2^\circ\text{K}$  reveals a rather sharp change in slope at 155 kOe. Although this result is in mild disagreement with the estimate in the short paper (200 kOe), the foundation for the new value appears stronger. On the negative side, measurements of the low field susceptibility as a function of temperature show a peak at about  $40^\circ\text{K}$ , only a few degrees higher than observed on the impure mineral, but far below the value of  $57^\circ\text{K}$  reported by Bizette for synthesized powder. At present no explanation of this discrepancy is known. Several possible alternatives are being examined.

An additional problem is connected to the high saturation moment per ferrous ion reported in the Conference paper at  $6\mu_B$ . Theoretically, a value close to  $6\mu_B$  is disconcerting, as was pointed out by Professor B. Bleaney during discussion of the oral Conference presentation of the paper. Within the experimental error, the lowest value may be  $5.7\mu_B$ . This number might be decreased still further to about  $5.6\mu_B$  by subtracting a contribution from the temperature independent paramagnetic susceptibility along the c-axis at  $4.2^\circ\text{K}$ . Its magnitude is taken equal to the value of at  $4.2^\circ\text{K}$ . Equivalent data on the analogous metamagnetic  $\text{FeCl}_2$  have not been clear in this respect. If a monocrystalline sample of the latter substance can be obtained, a check of its saturation per ferrous ion would be instructive.

#### 9. Antiferromagnetism of $\text{CoCl}_2$

During this contract period an investigation was started into the high magnetic field behavior of  $\text{CoCl}_2$ . This study is a joint project with Dr. S. Foner of the MIT National Magnet Laboratory, who has briefly noted his initial results in the Proceedings of the 1961 Conference on Magnetism and Magnetic Materials.(50) Considerable background data are available on this compound. The crystal structure is rhombohedral (which may also be treated as hexagonal, for convenience). It is isomorphous to  $\text{MnCl}_2$  (and  $\text{FeCl}_2$ ) having a layer structure of (0001) cation layers separated by two (0001) anion layers. Its magnetic ordering temperature is about  $25^\circ\text{K}$ , below which it is antiferromagnetic. The magnetic structure determined from neutron diffraction by Wilkinson, Cable, Wollan, and Koehler(51) indicates that the magnetic moments lie in the (0001) planes, all moments within a plane being parallel, and adjacent planes being antiparallel to each other. This compound has attracted experimental and theoretical interest for a long time in that many of its magnetic properties are field dependent (Refs. in Wilkinson *et al.*). The most notable example is the work of Starr, Bitter, and Kaufmann,(43) who measured the magnetization of a polycrystalline sample to about 30 kOe in the liquid hydrogen temperature range and above.

Single-crystal susceptibility measurements have also been obtained by Bizette and co-workers.<sup>(52)</sup> A recent study of the heat capacity and entropy by Chisholm and Stout,<sup>(53)</sup> complementing earlier work, indicates an entropy change associated with the ordering of  $R \ln 2$ .

The motivation for high field studies of  $\text{CoCl}_2$  lies in determining which of the various antiferromagnetic magnetization processes it will exhibit, and what parameters will be determined by observing such processes. The magnetic layer structure is characterized by a moderately strong ferromagnetic intralayer exchange and a relatively weak interlayer exchange. Some anisotropy of trigonal symmetry can be expected in the layer plane.

The initial experiments in this work comprised magnetization measurements at  $4.2^\circ$ ,  $20^\circ$ , and  $77^\circ\text{K}$  to 140 kOe with the field oriented perpendicular to the trigonal axis of a single crystal. This was intended to duplicate the measurements made by Foner.<sup>(50)</sup> Some nonlinearity of magnetization appeared under 10 kOe, as also observed by Foner, which corresponds to a domain reorientation against the in-plane anisotropy (low-field spin-flop) documented very clearly in the neutron diffraction work. Beyond this field range the susceptibility is constant to about 25 to 35 kOe, depending on the temperature, at which field the susceptibility drops rather sharply to a low but positive value, i.e., the magnetization becomes nearly flat. This process above 10 kOe is interpretable as the transverse magnetization in the (0001) plane and the saturation thereof. Some inkling of this saturation process is observable in the  $13.9^\circ\text{K}$  data of Starr *et al.* Ideally, on a good crystal the susceptibility above saturation should be nearly zero, except for possible excitation coupling with higher states.

A second, slightly better sample was purchased from Semi-Elements, Inc., Saxonburg, Pa. Magnetization measurements in the basal plane at  $4.2^\circ\text{K}$  to 200 kOe were qualitatively similar to the earlier ones, with the exception that the residual susceptibility above the "saturation" at 35 kOe is reduced from the earlier value but still appears to be present.

It is not clear yet whether these observations above 35 kOe are attributable to an excitation to higher states, or to some uncoupled paramagnetic contribution, possibly from a hydrated form of cobaltous chloride. The observations do not support the suggested negative susceptibility seen by Foner, which may have an instrumental origin. Very rough estimates of basal plane saturation are about  $2.2$  to  $2.3\mu$  per  $\text{Co}^{2+}$  corresponding to a  $g$  value of  $4.4$  to  $4.6$  for an effective  $S$  of  $1/2$ . This effective  $S$  is expected from crystal field theory and agrees with the magnetic entropy term.

Experiments were also attempted with the field along the  $c$ -axis, which is the hard direction of magnetization. The magnetization process expected is equivalent, but would require much larger fields to reach saturation. There is an additional stimulus in the possibility of observing an anisotropic saturation magnetization. [The theoretical work of Kanamori<sup>(46)</sup> also provides a helpful guide here, as in the case of  $\text{FeCO}_3$ .] To date,

saturation in this direction has not been attained owing to a catastrophic and irreversible rotation of the sample caused by magnetostatic torque in fields over 100 kOe. The sample appears to magnetize in the basal plane (despite a careful orientation) and simultaneously be turned by interaction with the field.

This investigation will be continued.

10. Magnetic Structure and Exchange  
in the Lanthanum Manganite Perovskites (ISJ, WLR)

The bulk of experimental work on this subject was carried out in the previous contract term and summarized in ASD Technical Report No. 61-630. Some discussion of this work has continued during the present contract period, and an abstract of a talk was presented at the American Physical Society meeting in St. Louis, March 25-28, 1963 as given below.

MAGNETIC EXCHANGE INTERACTIONS IN  
THE LANTHANUM MANGANITE SYSTEM

I. S. Jacobs and W. L. Roth  
General Electric Research Laboratory  
Schenectady, New York

The transition from antiferromagnetism (af) to ferromagnetism (f) in  $\text{La}(\text{Ba})\text{MnO}_3$  powders as  $[\text{Mn}^{+4}]$  increases from 0 to 30 per cent was studied by magnetization measurements to 150 kOe and neutron diffraction. Earlier analysis<sup>(54)</sup> invoked single-magnetic-axis structures and suggested an incoherent mixture of af and f phases within one crystallographic phase. An alternative suggestion<sup>(55)</sup> is that competition between double- and super-exchange creates a single-phase canted spin structure, whose interspin angle,  $\theta$ , varies with  $[\text{Mn}^{+4}]$ . The two-phase model predicts a high field susceptibility,  $\chi$ , that decreases as the spontaneous moment increases, whereas the cant model requires that  $\chi$  be nearly composition independent. Neutron data are compatible with both models; but magnetization data support the latter, ( $\chi_v \approx 8 \times 10^{-4}$ ), on samples whose spontaneous moment varies from 0 to 2/3 of ferromagnetic saturation. Interpreting the neutron scattering on the cant model, provisional values for  $\theta$  and the average moment/Mn site,  $\bar{M}$ , are 0° and  $3.7\beta$  for 30 per cent  $\text{Mn}^{+4}$  and 72° and  $3.1\beta$  for 18 per cent  $\text{Mn}^{+4}$ .

## REFERENCES

1. J. S. Kouvel, GE Research Lab. Rept. No. 57-RL-1799 (1957).
2. J. O. Artman, Phys. Rev., 105, 57 (1957).
3. C. D. Graham, J. Phys. Soc. Japan, 17, 1310 (1962).
4. A. F. Kip, Rev. Modern Phys., 25, 229 (1953).
5. S. Arajs and R. V. Colvin, J. Appl. Phys., 32, 336S (1961).
6. See, for instance, A. J. Freeman and R. E. Watson, Proc. Intern. Conf. on Magnetism, Kyoto, Japan (1961); J. Phys. Soc. Japan, 17, Supp. B-I, 15 (1962).
7. T. Kasuya, Progr. Theor. Phys. (Kyoto), 16, 45 (1956).
8. P. G. deGennes, Compt. rend., 247, 1836 (1958).
9. Bozorth, Matthias, Suhl, Corenzwit, and Davis, Phys. Rev., 115, 1595 (1959).
10. C. D. Graham, Jr., personal communication.
11. C. S. Gaskell and H. Motz, High Magnetic Fields, MIT and John Wiley and Sons, Inc., New York (1962), p. 565.
12. F. Barson, S. Legvold, and F. H. Spedding, Phys. Rev., 105, 418 (1957).
13. L. Patrick, Phys. Rev., 93, 384 (1954).
14. D. S. Rodbell, Phys. Rev. Letters, 7, 1 (1961).
15. C. P. Bean and D. S. Rodbell, Phys. Rev., 126, 104 (1962).
16. J. F. Smith, C. E. Carlson, and F. H. Spedding, J. Metals, 9, 1212 (1957).
17. F. C. Nix and D. MacNair, Phys. Rev., 60, 597 (1941).
18. Y. Kōi, A. Tsujimura, and T. Kushida, J. Phys. Soc. Japan, 15, 2100 (1960).
19. G. B. Benedek and J. Armstrong, J. Appl. Phys., 32, 106S (1961).
20. A. Tsujimura, F. Hihara, and Y. Kōi, J. Phys. Soc. Japan, 17, 1078 (1962).
21. T. Hihara, Y. Kōi, and A. Tsujimura, J. Phys. Soc. Japan, 17, 1320 (1962).
22. J. C. Fisher and I. Giaever, J. Appl. Phys., 32, 172 (1961).
23. I. Giaever and K. Megerle, Phys. Rev., 122, 1101 (1961).
24. K. Honda and T. Sone, Sci. Repts. Tohoku Imp. Univ., 3, 223 (1914).
25. I. E. Dzialoshinskii, J. Phys. Chem. Solids, 4, 241 (1958).

27. C. G. Shull, W. A. Strauser, and E. A. Wollan, Phys. Rev., 83, 333 (1951).
28. A. Aharoni, E. H. Frei, and M. Schieber, unpublished work communicated by Dr. Aharoni; Phys. Rev., 127, 439 (1962).
29. S. Freier, M. Greenshpan, P. Hellman, and H. Shechter, Phys. Letters, 2, 191 (1962).
30. G. Foëx, Compt. rend., 227, 193 (1948).
31. G. Chaudron and H. Forestier, Compt. rend., 179, 763 (1924).
32. B. T. M. Willis and H. P. Rooksby, Proc. Phys. Soc. (London), B65, 950 (1952).
33. P. W. Bridgman, Proc. Am. Acad. Arts Sci., 77, 187 (1949).
34. American Institute of Physics Handbook, McGraw-Hill Book Co., Inc., New York (1957), pp. 2-57.
35. E. L. Boyd, L. J. Bruner, J. I. Budnick, and R. J. Blume, Bull. Am. Phys. Soc., 6, 159 (1961).
36. G. G. Robbrecht and R. J. Doclo, Phys. Letters, 3, 85 (1962).
37. M. Foëx, Ann. Phys., 16, 174 (1921).
38. J. Becquerel and W. J. deHaas, Leiden Comm. Suppl. No. 81a to Nos. 241-252 (1936).
39. H. Bizette, J. phys. radium, 12, 161 (1951).
40. R. A. Alikhanov, Soviet Phys.-JETP, 9, 1204 (1959).
41. S. J. Pickart, Bull. Am. Phys. Soc., 5, 357 (1960).
42. L. Néel, Inst. intern. phys. Solvay, 10th Conseil phys., 251 (1955).
43. C. Starr, F. Bitter, and A. R. Kaufmann, Phys. Rev., 58, 977 (1940).
44. H. Bizette, C. Terrier, and B. Tsai, Compt. rend., 243, 895 (1956).
45. N. M. Kreines, Soviet Phys.-JETP, 13, 534 (1961).
46. J. Kanamori, Progr. Theoret. Phys., 20, 890 (1958).
47. I. S. Jacobs and P. E. Lawrence, Rev. Sci. Instr., 29, 713 (1958); improved by substitution of electronic integrators.
48. I. S. Jacobs, J. Appl. Phys., 32, 61S (1961).
49. B. R. Heap, Proc. Phys. Soc., 80, 248 (1962).
50. S. Foner and S. L. Hou, J. Appl. Phys. Suppl., 33, 1289 (1962).
51. M. K. Wilkinson, J. W. Cable, E. O. Wollan, and W. C. Koehler, Phys. Rev., 113, 497 (1959).
52. H. Bizette, C. Terrier, and B. Tsai, Compt. rend., 243, 1295 (1956).

53. R.C. Chisholm and J.W. Stout, J. Chem. Phys., 36, 972 (1962).
54. E.O. Wollan and W.C. Koehler, Phys. Rev., 100, 545 (1955).
55. P.G. de Gennes, Phys. Rev., 118, 141 (1960).

<p>1. Microstructure 2. Magnetic fields 3. Ferromagnetism 4. Antiferromagnetism</p> <p>I. Aeronautical Systems Division, Dir/Materials and Processes, Physics Lab, Wright-Patterson AFB, Ohio.</p> <p>Rpt Nr ASD-TDR-63-208. RESEARCH AND DEVELOPMENT TO INVESTIGATE THE MICROSTRUCTURE OF THE INTERNAL MAGNETIC FIELD IN FERRO-, FERRI-, AND ANTI-FERROMAGNETIC SOLIDS. Final report, Apr 63, 28p. Incl illus., tables, 55 refs.</p> <p>Unclassified Report</p> <p>Research dealing with fundamental interactions and the microstructure of internal fields in selected magnetic materials is</p>	<p>1. Microstructure 2. Magnetic fields 3. Ferromagnetism 4. Antiferromagnetism</p> <p>I. AFSC Project 7371 Task 737103</p> <p>II. Contract AF 33 (657)-3462</p> <p>III. General Electric Co., Schenectady, New York</p> <p>IV. D.S. Rodbell, et al.</p> <p>V. Aval for OTS</p> <p>VI. In ASTIA collection</p>
<p>( over )</p>	<p>( over )</p>

described. Static and microwave magnetic properties of single-crystal gadolinium are under investigation. Thermal expansion data of several ferromagnetic metals and one antiferromagnetic oxide are discussed. Cobalt particles precipitated in a copper-cobalt alloy are under study by nuclear resonance and ferromagnetic resonance for separate metallurgically oriented goals. Nuclear resonance studies of MnAs are reported and exploration commenced on electron tunnelling into ferromagnetic alloys. High field studies of magnetization processes in the antiferromagnetic compounds,  $FeCO_3$  and  $CoCl_2$ , are also reported.

described. Static and microwave magnetic properties of single-crystal gadolinium are under investigation. Thermal expansion data of several ferromagnetic metals and one antiferromagnetic oxide are discussed. Cobalt particles precipitated in a copper-cobalt alloy are under study by nuclear resonance and ferromagnetic resonance for separate metallurgically oriented goals. Nuclear resonance studies of MnAs are reported and exploration commenced on electron tunnelling into ferromagnetic alloys. High field studies of magnetization processes in the antiferromagnetic compounds,  $FeCO_3$  and  $CoCl_2$ , are also reported.

<p>1. Microstructure 2. Magnetic fields 3. Ferromagnetism 4. Antiferromagnetism</p> <p>I. AFSC Project 7371 Task 737103 Contract AF 33 (657)-8462</p> <p>II. General Electric Co., Schenectady, New York</p> <p>III. D.S. Rodbell, et al. Aval fr OTS In ASTIA collection</p>	<p>I. Microstructure 2. Magnetic fields 3. Ferromagnetism 4. Antiferromagnetism I. AFSC Project 7371 Task 737103 Contract AF 33 (657)-8462</p> <p>II. General Electric Co., Schenectady New York</p> <p>III. D.S. Rodbell, et al. Aval fr OTS In ASTIA collection</p>
<p>1. Microstructure 2. Magnetic fields 3. Ferromagnetism 4. Antiferromagnetism</p> <p>I. AFSC Project 7371 Task 737103 Contract AF 33 (657)-8462</p> <p>II. General Electric Co., Schenectady, New York</p> <p>III. D.S. Rodbell, et al. Aval fr OTS In ASTIA collection</p>	<p>1. Microstructure 2. Magnetic fields 3. Ferromagnetism 4. Antiferromagnetism I. AFSC Project 7371 Task 737103 Contract AF 33 (657)-8462</p> <p>II. General Electric Co., Schenectady New York</p> <p>III. D.S. Rodbell, et al. Aval fr OTS In ASTIA collection</p>

Aeronautical Systems Division, Dir/Materials and Processes, Physics Lab, Wright-Patterson AFB, Ohio.

Rpt Nr ASD-TDR-63-208. RESEARCH AND DEVELOPMENT TO INVESTIGATE THE MICROSTRUCTURE OF THE INTERNAL MAGNETIC FIELD IN FERRO-, FERRI-, AND ANTIFERROMAGNETIC SOLIDS. Final report, Apr 63, 28p. Incl illus., tables, 55 refs.

Unclassified Report

Research dealing with fundamental interactions and the microstructure of internal fields in selected magnetic materials is

(over)

described. Static and microwave magnetic properties of single-crystal gadolinium are under investigation. Thermal expansion data of several ferromagnetic metals and one antiferromagnetic oxide are discussed. Cobalt particles precipitated in a copper-cobalt alloy are under study by nuclear resonance and ferromagnetic resonance for separate metallurgically oriented goals. Nuclear resonance studies of MnAs are reported and exploration commenced on electron tunnelling into ferromagnetic alloys. High field studies of magnetization processes in the antiferromagnetic compounds,  $\text{FeCO}_3$  and  $\text{CoCl}_2$  are also reported.

(over)

described. Static and microwave magnetic properties of single-crystal gadolinium are under investigation. Thermal expansion data of several ferromagnetic metals and one antiferromagnetic oxide are discussed. Cobalt particles precipitated in a copper-cobalt alloy are under study by nuclear resonance and ferromagnetic resonance for separate metallurgically oriented goals. Nuclear resonance studies of MnAs are reported and exploration commenced on electron tunnelling into ferromagnetic alloys. High field studies of magnetization processes in the antiferromagnetic compounds,  $\text{FeCO}_3$  and  $\text{CoCl}_2$  are also reported.

<p>1. Microstructure 2. Magnetic fields 3. Ferromagnetism 4. Antiferromagnetism</p> <p>I. Rpt Nr ASD-TDR-63-208. RESEARCH AND DEVELOPMENT TO INVESTIGATE THE MICROSTRUCTURE OF THE INTERNAL MAGNETIC FIELD IN FERRO-, FERRI-, AND ANTIFERROMAGNETIC SOLIDS. Final report, Apr 63, 28p. Incl illus., tables, 55 refs.</p> <p>Unclassified Report</p> <p>Research dealing with fundamental interactions and the microstructure of internal fields in selected magnetic materials is</p>	<p>Aeronautical Systems Division, Dir/Materials and Processes, Physics Lab, Wright-Patterson AFB, Ohio.</p> <p>AFSC Project 7371 Task 737103 Contract: AF 33 (657)-8462</p> <p>III. General Electric Co., Schenectady, New York</p> <p>IV. D.S. Rodbell, et al.</p> <p>V. Aval fr OTS</p> <p>VI. In ASTIA collection</p> <p>1. Microstructure 2. Magnetic fields 3. Ferromagnetism 4. Antiferromagnetism</p> <p>I. AFSC Project 7371 Task 737103 Contract AF 33 (657)-8462</p> <p>II. General Electric Co., Schenectady, New York</p> <p>IV. D.S. Rodbell, et al.</p> <p>V. Aval fr OTS</p> <p>VI. In ASTIA collection</p>
<p>(over)</p> <p>(over)</p>	<p>described. Static and microwave magnetic properties of single-crystal gadolinium are under investigation. Thermal expansion data of several ferromagnetic metals and one antiferromagnetic oxide are discussed. Cobalt particles precipitated in a copper-cobalt alloy are under study by nuclear resonance and ferromagnetic resonance for separate metallurgically oriented goals. Nuclear resonance studies of MnAs are reported and exploration commenced on electron tunnelling into ferromagnetic alloys. High field studies of magnetization processes in the antiferromagnetic compounds, <math>FeCO_3</math> and <math>CoCl_2</math>, are also reported.</p> <p>(over)</p>

<p>1. Microstructure 2. Magnetic fields 3. Ferromagnetism 4. Antiferromagnetism</p> <p>I. AFSC Project 7371 Task 737103 Contract AF 33 (657)-8462</p> <p>II. Contract AF 33 (657)-8462</p> <p>III. General Electric Co., Schenectady, New York</p> <p>IV. D.S. Rodbell, et al. Aval fr OTS</p> <p>V. Unclassified Report Research dealing with fundamental interactions and the microstructure of internal fields in selected magnetic materials is</p>	<p>Aeronautical Systems Division, Dir/Materials and Processes, Physics Lab, Wright-Patterson AFB, Ohio. Rpt Nr ASD-TDR-63-208. RESEARCH AND DEVELOPMENT TO INVESTIGATE THE MICROSTRUCTURE OF THE INTERNAL MAGNETIC FIELD IN FERRO-, FERRI-, AND ANTI-FERROMAGNETIC SOLIDS. Final report, Apr 63, 28p. incl illus., tables, 55 refs.</p> <p>Unclassified Report Research dealing with fundamental interactions and the microstructure of internal fields in selected magnetic materials is</p> <p>1. Microstructure 2. Magnetic fields 3. Ferromagnetism 4. Antiferromagnetism</p> <p>I. AFSC Project 7371 Task 737103 Contract AF 33 (657)-8462</p> <p>II. Contract AF 33 (657)-8462</p> <p>III. General Electric Co., Schenectady, New York</p> <p>IV. D.S. Rodbell, et al. Aval fr OTS</p> <p>V. Unclassified Report Research dealing with fundamental interactions and the microstructure of internal fields in selected magnetic materials is</p>
<p>1. Microstructure 2. Magnetic fields 3. Ferromagnetism 4. Antiferromagnetism</p> <p>I. AFSC Project 7371 Task 737103 Contract AF 33 (657)-8462</p> <p>II. Contract AF 33 (657)-8462</p> <p>III. General Electric Co., Schenectady, New York</p> <p>IV. D.S. Rodbell, et al. Aval fr OTS</p> <p>V. Unclassified Report Research dealing with fundamental interactions and the microstructure of internal fields in selected magnetic materials is</p> <p>( over )</p>	<p>described. Static and microwave magnetic properties of single-crystal gadolinium are under investigation. Thermal expansion data of several ferromagnetic metals and one antiferromagnetic oxide are discussed. Cobalt particles precipitated in a copper-cobalt alloy are under study by nuclear resonance and ferromagnetic resonance for separate metallurgically oriented goals. Nuclear resonance studies of MnAs are reported and exploration commenced on electron tunneling into ferromagnetic alloys. High field studies of magnetization processes in the antiferromagnetic compounds, <math>FeO_3</math> and <math>CoCl_2</math> are also reported.</p> <p>( over )</p>

<p>1. Microstructure 2. Magnetic fields 3. Ferromagnetism 4. Antiferromagnetism</p> <p>I. AFSC Project 7371 Task 737103</p> <p>II. Contract AF 33 (657)-8462</p> <p>III. General Electric Co., Schenectady, New York</p> <p>IV. D.S. Rodbell, et.al. Aval fr OTS</p> <p>V. In ASTIA collection</p> <p>VI. In ASTIA collection</p>	<p>Aeronautical Systems Division, Dir/Materials and Processes, Physics Lab, Wright-Patterson AFB, Ohio.</p> <p>Rpt Nr ASD-TDR-63-208. RESEARCH AND DEVELOPMENT TO INVESTIGATE THE MICROSTRUCTURE OF THE INTERNAL MAGNETIC FIELD IN FERRO-, FERRI-, AND ANTI FERROMAGNETIC SOLIDS. Final report, Apr 63, 28p. Incl illus., tables, 55 refs.</p> <p>Unclassified Report</p> <p>Research dealing with fundamental interactions and the microstructure of internal fields in selected magnetic materials is</p>	<p>1. Microstructure 2. Magnetic fields 3. Ferromagnetism 4. Antiferromagnetism</p> <p>I. AFSC Project 7371 Task 737103</p> <p>II. Contract AF 33 (657)-8462</p> <p>III. General Electric Co., Schenectady, New York</p> <p>IV. D.S. Rodbell, et.al. Aval fr OTS</p> <p>V. In ASTIA collection</p> <p>VI. In ASTIA collection</p>
<p>1. Microstructure 2. Magnetic fields 3. Ferromagnetism 4. Antiferromagnetism</p> <p>I. AFSC Project 7371 Task 737103</p> <p>II. Contract AF 33 (657)-8462</p> <p>III. General Electric Co., Schenectady, New York</p> <p>IV. D.S. Rodbell, et.al. Aval fr OTS</p> <p>V. In ASTIA collection</p> <p>VI. In ASTIA collection</p>	<p>1. Microstructure 2. Magnetic fields 3. Ferromagnetism 4. Antiferromagnetism</p> <p>I. AFSC Project 7371 Task 737103</p> <p>II. Contract AF 33 (657)-8462</p> <p>III. General Electric Co., Schenectady, New York</p> <p>IV. D.S. Rodbell, et.al. Aval fr OTS</p> <p>V. In ASTIA collection</p> <p>VI. In ASTIA collection</p>	<p>(over)</p>

described. Static and microwave magnetic properties of single-crystal gadolinium are under investigation. Thermal expansion data of several ferromagnetic metals and one antiferromagnetic oxide are discussed. Cobalt particles precipitated in a copper-cobalt alloy are under study by nuclear resonance and ferromagnetic resonance for separate metallurgically oriented goals. Nuclear resonance studies of MnAs are reported and exploration commenced on electron tunneling into ferromagnetic alloys. High field studies of magnetization processes in the antiferromagnetic compounds,  $\text{FeCO}_3$  and  $\text{CoCl}_2$  are also reported.

described. Static and microwave magnetic properties of single-crystal gadolinium are under investigation. Thermal expansion data of several ferromagnetic metals and one antiferromagnetic oxide are discussed. Cobalt particles precipitated in a copper-cobalt alloy are under study by nuclear resonance and ferromagnetic resonance for separate metallurgically oriented goals. Nuclear resonance studies of MnAs are reported and exploration commenced on electron tunneling into ferromagnetic alloys. High field studies of magnetization processes in the antiferromagnetic compounds,  $\text{FeCO}_3$  and  $\text{CoCl}_2$  are also reported.

(over)

Aeronautical Systems Division, Dir/Materials and Processes, Physics Lab, Wright-Patterson AFB, Ohio.  
Rpt Nr ASD-TDR-63-208. RESEARCH AND DEVELOPMENT TO INVESTIGATE THE MICROSTRUCTURE OF THE INTERNAL MAGNETIC FIELD IN FERRO-, FERRI-, AND ANTI FERROMAGNETIC SOLIDS. Final report, Apr 63, 28p. incl illus., tables, 55 refs.

Unclassified Report

Research dealing with fundamental interactions and the microstructure of internal fields in selected magnetic materials is

1. Microstructure
2. Magnetic fields
3. Ferromagnetism
4. Antiferromagnetism
- I. AFSC Project 7371
- Task 737103
- Contract AF 33
- II. (657)-8462
- III. General Electric Co., Schenectady, New York
- D. S. Rodbell, et al.
- Aval fr OTS
- In ASTIA collection

{ over }

Aeronautical Systems Division, Dir/Materials and Processes, Physics Lab, Wright-Patterson AFB, Ohio.  
Rpt Nr ASD-TDR-63-208. RESEARCH AND DEVELOPMENT TO INVESTIGATE THE MICROSTRUCTURE OF THE INTERNAL MAGNETIC FIELD IN FERRO-, FERRI-, AND ANTI FERROMAGNETIC SOLIDS. Final report, Apr 63, 28p. incl illus., tables, 55 refs.

Unclassified Report

Research dealing with fundamental interactions and the microstructure of internal fields in selected magnetic materials is

{ over }

1. Microstructure
2. Magnetic fields
3. Ferromagnetism
4. Antiferromagnetism
- I. AFSC Project 7371
- Task 737103
- Contract AF 33
- II. (657)-8462
- III. General Electric Co., Schenectady, New York
- D. S. Rodbell, et al.
- Aval fr OTS
- In ASTIA collection

{ over }

described. Static and microwave magnetic properties of single-crystal gadolinium are under investigation. Thermal expansion data of several ferromagnetic metals and one antiferromagnetic oxide are discussed. Cobalt particles precipitated in a copper-cobalt alloy are under study by nuclear resonance and ferromagnetic resonance for separate metallurgically oriented goals. Nuclear resonance studies of MnAs are reported and exploration commenced on electron tunnelling into ferromagnetic alloys. High field studies of magnetization processes in the antiferromagnetic compounds,  $FeCO_3$  and  $CoCl_2$  are also reported.

described. Static and microwave magnetic properties of single-crystal gadolinium are under investigation. Thermal expansion data of several ferromagnetic metals and one antiferromagnetic oxide are discussed. Cobalt particles precipitated in a copper-cobalt alloy are under study by nuclear resonance and ferromagnetic resonance for separate metallurgically oriented goals. Nuclear resonance studies of MnAs are reported and exploration commenced on electron tunnelling into ferromagnetic alloys. High field studies of magnetization processes in the antiferromagnetic compounds,  $FeCO_3$  and  $CoCl_2$  are also reported.